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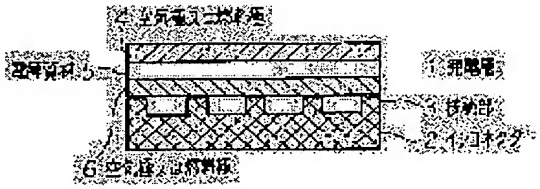
(54) SOLID ELECTROLYTE CELL AND MANUFACTURE THEREOF

(57)Abstract:
PURPOSE: To reduce the contact resistance and the cost and increase the mass- productivity, by interposing a porous material thin film between the interconnector having grooves and the power generation layer.
CONSTITUTION: A power generation layer 1 is prepared by laminating an electrolytic material 5, and a fuel pole or an air pole 4 or 6 and bonding them to each other. An interconnector 2 is formed by extrusion technique and is bonded to the resulting laminate body. A connection portion 3 is prepared using a sheet with a doctor blade process, and this connection portion 3 is interposed between the powder generation layer 1 and the interconnector 2 and is filled between both. The interconnector 2 has grooves at its surface contacting with the power generation layer 1, which grooves are intended to supply air or fuel while, on the other hand, the sheet is porous material thin film which consists of a fuel pole material or air material. This improves the electrical connection between the power generation layer 1 and the interconnector 2, and makes the contact resistance low, thus enabling mass-production of a high-performance and inexpensive cell.



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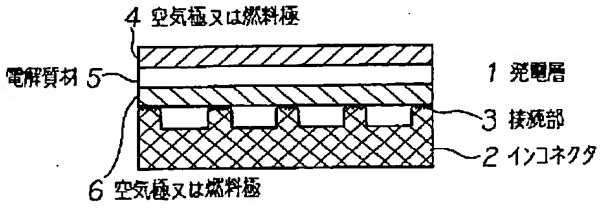
(54)【発明の名称】　固体電解質セル及びその製造方法

(57)【要約】

【目的】　高温水電解装置、固体電解質型燃料電池などに有利に適用される固体電解質セル及びその製造方法に関する。

【構成】　発電層とインタコネクタの接続面に発電層電極材（燃料極材又は空気極材）をシート状に加工し未焼結の状態で充てんした後、焼結を行なうことにより発電層／インタコネクタ間の接着性を向上させ界面抵抗を低減できるようにした固体電解質セル及びその製造方法。



1

【特許請求の範囲】

【請求項１】　燃料極材と電解質材と空気極材とからなる発電層と、該発電層に接する面に開口された燃料又は空気を供給する溝を有するインタコネクタと、該インタコネクタと前記発電層との接合部に介在させた燃料極材又は空気極材よりなる多孔質体の薄膜とを具備してなることを特徴とする固体電解質セル。

【請求項２】　燃料極材と電解質材と空気極材とからなる発電層と、該発電層に接する面に開口された燃料又は空気を供給する溝を有するインタコネクタとの接合部に燃料極材又は空気極材の多孔質体の薄膜を挟持させる第１の工程と、前記多孔質体を挟持した前記発電層及び前記インタコネクタをその挟持面に荷重をかけながら焼結させる第２の工程とを有してなることを特徴とする固体電解質セルの製造方法。

【発明の詳細な説明】

【０００１】

【産業上の利用分野】本発明は高温水電解装置、固体電解質型燃料電池（以下、これをＳＯＦＣと略す）などに有利に適用される固体電解質セル及びその製造方法に関する。

【０００２】

【従来の技術】ＳＯＦＣは燃料に含有される化学エネルギを燃焼による熱エネルギの形態を経由することなく電気化学的手段を利用して等温下で連続的に電気エネルギへ直接変換する装置でカルノー効率の制約を受けないため本質的に高いエネルギ変換率を有し、更に良好な環境保全性が期待されるなどの特徴を有している。

【０００３】平板型ＳＯＦＣでは、図１を参照して説明すると、発電を行なう発電層１（燃料極と電解質材と空気極よりなる）と、供給ガスの混入を避け、かつ電気を流すセパレータ（インタコネクタ）２とからなり、発電層１とインタコネクタ２の接続部３は、機械的な押し付けあるいは白金黒等易焼結性貴金属のペーストを塗布した後の焼結により行なわれている。

【０００４】

【発明が解決しようとする課題】しかしながら、発電層、インタコネクタともに接続部は微視的には５０～１００μｍ程度湾曲しており、従来技術では良好な接続を得ることが難しく、接続部での接触抵抗が大きく性能低下の原因となっている。例えば機械的な押し付けでは高精度の制御が必要であり、セルの破損を生じやすい。一方、貴金属ペーストの塗布では原料が高価であり、また均一な塗布面が得られない。

【０００５】本発明は上記技術水準に鑑み、接触抵抗が小さい接続が可能で、かつ安価で量産性に富む固体電解質セル及びその製造方法を提供しようとするものである。

【０００６】

【課題を解決するための手段】本発明は

2

（１）燃料極材と電解質材と空気極材とからなる発電層と、該発電層に接する面に開口された燃料又は空気を供給する溝を有するインタコネクタと、該インタコネクタと前記発電層との接合部に介在させた燃料極材又は空気極材よりなる多孔質体の薄膜とを具備してなることを特徴とする固体電解質セル。

【０００７】（２）燃料極材と電解質材と空気極材とからなる発電層と、該発電層に接する面に開口された燃料又は空気を供給する溝を有するインタコネクタとの接合部に燃料極材又は空気極材の多孔質体の薄膜を挟持させる第１の工程と、前記多孔質体を挟持した前記発電層及び前記インタコネクタをその挟持面に荷重をかけながら焼結させる第２の工程とを有してなることを特徴とする固体電解質セルの製造方法。

である。

【０００８】すなわち、本発明は発電層とインタコネクタの接続面に発電層電極材（燃料極材または空気極材）をシート状に加工し未焼結の状態で充てんした後、焼結を行なうことにより発電層／インタコネクタ間の接着性を向上させ界面抵抗を低減できるようにした固体電解質セル及びその製造方法である。

【０００９】上記において、発電層の電極材のシート状への加工は従来一般的に使われているセラミックスの薄膜成形方法（ドクターブレード法、カレンダーロール法、押し出し法）により行なえばよい。これらの方法により作成された薄膜は焼結前にはセラミックス粉の他に有機バインダを含有して可塑性に富んでいるので発電層とインタコネクタ間に置き、適度に加圧することにより発電層、インタコネクタの湾曲部に充てんされる。シート状に加工する際に使用される有機バインダは用いられる粉体の性状、分散剤、溶媒によって変わるが、一般的にポリメチルアクリレート、ニトロセルロース、ポリエチレン、石油樹脂、ポリビニルアルコール、ポリビニルブチラール樹脂、ポリ塩化ビニル、アクリル酸ポリマ、メタクリル酸ポリマ、メチルセルロース、ワックスなどが使用される。

【００１０】

【作用】本発明によれば、従来と比べ、発電層とインタコネクタ間の電気的な接続が良好となり、高性能な固体電解質セルを提供することが可能となる。

【００１１】

【実施例】以下、図１により、本発明の一実施例を従来の態様のものと比較して説明し、本発明の効果を立証する。

【００１２】発電層１の構成膜としての電解質材５はイットリア安定化ジルコニアを、燃料極４又は６はＮｉ／ZrO_2サーメットを、空気極４又は６は$LaSrMnO_3$を使用し、各々の膜はドクターブレード法により成膜した。これを積層した後、焼結を行ない発電層１を作成した。またインタコネクタ２としてはＬａＣｒＭｇＯ

$_3$を使用し、これは押し出し法により成形し焼結した。

【００１３】両者の接続面に充てんするシートもドクターブレード法により作成し、材料は空気極材であるＬａＳｒＭｎＯ$_3$を使用した。またこのとき可塑性を保持させるために有機バインダとしてアクリル樹脂とフタル酸のエステルを５～１５％添加した。

【００１４】発電層１とインタコネクタ２の接続は１．５～１０ｇ／ｃｍ^{2}の荷重をかけ１０００～１４００℃の温度で加熱して行なった。

【００１５】このようにして得た発電層／インタコネクタ接続体を直流四端子法により電気抵抗を測定した。＊

＊【００１６】また比較として機械的に押し付けたもの、接続面に貴金属（白金黒）ペーストを塗布、焼結（１０００℃）したものについても同様に測定した。

【００１７】結果を表１及び表２に示す。シート状の接続層を設けたものは機械的な押し付けや白金ペーストに比べて、発電層／インタコネクタの界面抵抗は小さく、特に１２００～１３００℃の温度で加熱し、また荷重量は４．０ｇ／ｃｍ^{2}以上のとき界面抵抗は小さくなることが確認された。

【表１】

表　１

接着温度（℃）	界面抵抗（Ω・ｃｍ^2）
１０００	１２．０
１０００＊	４．２×１０$^{-1}$
１１００	２．３
１２００	６．０×１０$^{-2}$
１２００＊	１．１
１３００	５．８×１０$^{-2}$
１４００	１．８

（荷重量　６．０ｇ／ｃｍ^2）

＊はＰｔペーストを使用

【表２】

表　２

荷重量（ｇ／ｃｍ^2）	界面抵抗（Ω・ｃｍ^2）
１．５	９．３×１０$^{-1}$
３．０	２．８×１０$^{-1}$
４．０	６．４×１０$^{-2}$
６．０	６．０×１０$^{-2}$
８．０	５．７×１０$^{-2}$
１０．０	５．９×１０$^{-2}$

（接着温度　１２００℃）

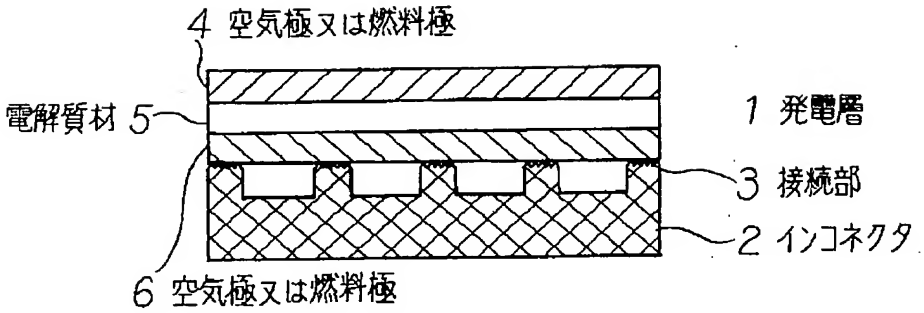
【００１８】

【発明の効果】本発明によれば、発電層とインタコネクタ間の電気的接続が良好となり、高性能の固体電解質セルを提供することが可能となる。

【図面の簡単な説明】

【図１】平板型固体電解質型燃料電池の構成の説明図。

【図１】



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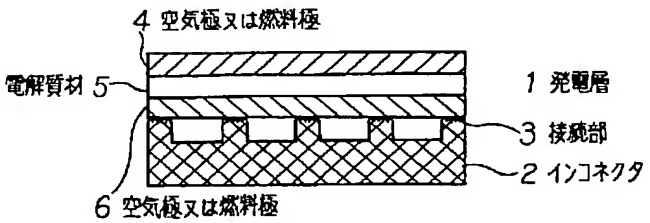
CLAIMS

[Claim(s)]
[Claim 1] The solid electrolyte cel characterized by coming to provide the thin film of the porous body which consists of the fuel electrode material or air pole material made to be placed between the joints of the interconnector which has the slot which supplies the fuel or air by which opening was carried out to the field which touches the generation-of-electrical-energy layer which consists of fuel electrode material, electrolyte material, and air pole material, and this generation-of-electrical-energy layer, and a this interconnector and said generation-of-electrical-energy layer.
[Claim 2] The 1st process which makes a joint with the interconnector which has the slot which supplies the fuel or air by which opening was carried out to the field which touches the generation-of-electrical-energy layer which consists of fuel electrode material, electrolyte material, and air pole material, and this generation-of-electrical-energy layer pinch the thin film of the porous body of fuel electrode material or air pole material, The manufacture approach of the solid electrolyte cel characterized by coming to have the 2nd process which makes said generation-of-electrical-energy layer to which said porous body was pinched, and said interconnector sinter, applying a load to the pinching side.

[Translation done.]

Drawing selection Representative drawing



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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the solid electrolyte cel applied in favor of a high-temperature-hot-water electrolytic device, a solid oxide fuel cell (this is hereafter abbreviated to SOFC), etc., and its manufacture approach.
[0002]
[Description of the Prior Art] SOFC essentially has a high rate of energy conversion in order not to receive constraint of the Carnot efficiency with the equipment which carries out direct conversion to electrical energy continuously under isothermal using an electrochemical means, without going via the gestalt of the heat energy according the chemical energy contained to a fuel to combustion, and it has the description of still better environmental preservation nature being expected.
[0003] In the monotonous mold SOFC, if it explains with reference to drawing 1 , it consists of a separator (interconnector) 2 which avoids the generation-of-electrical-energy layer 1 (it consists of a fuel electrode, electrolyte material, and an air pole) which generates electricity, and mixing of distributed gas, and passes the electrical and electric equipment, and the connection 3 of the generation-of-electrical-energy layer 1 and an interconnector 2 is performed by sintering after [mechanical] pushing or applying the paste of sinterable nature noble metals, such as platinum black.
[0004]
[Problem(s) to be Solved by the Invention] However, as for a connection, a generation-of-electrical-energy layer and about 50-100 micrometers of interconnectors are curving microscopically, it is difficult to obtain good connection with the conventional technique, and the contact resistance in a connection causes degradation greatly. For example, in mechanical forcing, highly precise control is required and it is easy to produce breakage of a cel. On the other hand, in spreading of a noble-metals paste, the spreading side where a raw material is uniform at an expensive price is not acquired.
[0005] This invention tends to offer the solid electrolyte cel which connection with small contact resistance is possible, and is cheap, and is rich in mass-production nature in view of the above-mentioned technical level, and its manufacture approach.
[0006]
[Means for Solving the Problem] This invention is a solid electrolyte cel characterized by coming to provide the thin film of the porous body which consists of the fuel electrode material or air pole material made to be placed between the joints of the interconnector which has the slot which supplies the fuel or air by which opening was carried out to the field which touches the generation-of-electrical-energy layer which consists of (1) fuel-electrode material, electrolyte material, and air pole material, and this generation-of-electrical-energy layer, and a this interconnector and said generation-of-electrical-energy layer.
[0007] (2) The 1st process which makes a joint with the interconnector which has the slot which supplies the fuel or air by which opening was carried out to the field which touches the generation-of-electrical-energy layer which consists of fuel electrode material, electrolyte material, and air pole material, and this generation-of-electrical-energy layer pinch the thin film of the porous body of fuel electrode material or air pole material, The manufacture approach of the solid electrolyte cel characterized by coming to have the 2nd process which makes said generation-of-electrical-energy layer to which said porous body was pinched, and said interconnector sinter, applying a load to the pinching side.
It comes out.
[0008] That is, after it processes generation-of-electrical-energy layer electrode material (fuel electrode material or air

pole material) on the connection side of a generation-of-electrical-energy layer and an interconnector in the shape of a sheet and this invention fills it up into it with the condition of not sintering, they are the solid electrolyte cel which the adhesive property between a generation-of-electrical-energy layer / interconnector is raised, and enabled it to reduce interfacial resistance, and its manufacture approach by performing sintering.
[0009] What is necessary is just to perform processing to the shape of a sheet of the electrode material of a generation-of-electrical-energy layer in the above by the thin film shaping approach (a doctor blade method, the calendering roll method, extrusion process) of the ceramics currently generally used conventionally. Since the thin film created by these approaches contains the organic binder other than ceramic powder before sintering and is rich in plasticity, it is placed between a generation-of-electrical-energy layer and an interconnector, and the bend of a generation-of-electrical-energy layer and an interconnector is filled up with it by pressurizing moderately. Although the organic binder used changes with the description of the fine particles used, a dispersant, and a solvent in case it is processed in the shape of a sheet, generally polymethyl acrylate, a nitrocellulose, polyethylene, petroleum resin, polyvinyl alcohol, polyvinyl butyral resin, a polyvinyl chloride, an acrylic-acid polymer, a methacrylic-acid polymer, methyl cellulose, a wax, etc. are used.
[0010]
[Function] According to this invention, compared with the former, the electric connection between a generation-of-electrical-energy layer and an interconnector becomes good, and it becomes possible to offer a highly efficient solid electrolyte cel.
[0011]
[Example] Hereafter, by drawing 1 , one example of this invention is explained as compared with the thing of the conventional mode, and the effectiveness of this invention is proved.
[0012] For the electrolyte material 5 as configuration film of the generation-of-electrical-energy layer 1, a fuel electrode 4 or 6 is yttria stabilized zirconia nickel/ZrO2 About a cermet, an air pole 4 or 6 is LaSrMnO3. It was used and each film formed membranes with the doctor blade method. After carrying out the laminating of this, sintering was performed and the generation-of-electrical-energy layer 1 was created. Moreover, as an interconnector 2, it is LaCrMgO3. It was used, and this was fabricated with the extrusion process and sintered.
[0013] It is LaSrMnO3 whose ingredient the sheet with which both connection side is filled up is also created with a doctor blade method, and is air pole material. It was used. Moreover, in order to make plasticity hold at this time, the ester of acrylic resin and a phthalic acid was added 5 to 15% as an organic binder.
[0014] Connection of the generation-of-electrical-energy layer 1 and an interconnector 2 is 1.5 - 10 g/cm2. It carried out by applying a load and heating at the temperature of 1000-1400 degrees C.
[0015] Thus, electric resistance was measured for the acquired generation-of-electrical-energy layer / interconnector connection object with the direct-current four probe method.
[0016] Moreover, it measured similarly about what applied the noble-metals (platinum black) paste to the thing and connection side which were mechanically forced as a comparison, and was sintered (1000 degrees C).
[0017] A result is shown in Table 1 and 2. Compared with forcing with what [mechanical] prepared the sheet-like connection layer, or a platinum paste, the interfacial resistance of a generation-of-electrical-energy layer / interconnector is small, and it heats at the temperature of 1200-1300 degrees C especially, and the amount of loads is 4.0 g/cm2. It was checked at the above time that interfacial resistance becomes small.
[Table 1]

表　1

接着温度（℃）	界面抵抗（Ω・cm²）
1000	12.0
1000*	4.2×10^{-1}
1100	2.3
1200	6.0×10^{-2}
1200*	1.1
1300	5.8×10^{-2}
1400	1.8

（荷重量　6.0g／cm²）

* はPtペーストを使用

[Table 2]

表　2

荷重量（g／cm²）	界面抵抗（Ω・cm²）
1.5	9.3×10^{-1}
3.0	2.8×10^{-1}
4.0	6.4×10^{-2}
6.0	6.0×10^{-2}
8.0	5.7×10^{-2}
10.0	5.9×10^{-2}

（接着温度　1200℃）

[0018]
[Effect of the Invention] According to this invention, the electrical installation between a generation-of-electrical-energy layer and an interconnector becomes good, and it becomes possible to offer the solid electrolyte cel of high performance.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] The explanatory view of the configuration of a monotonous mold solid oxide fuel cell.

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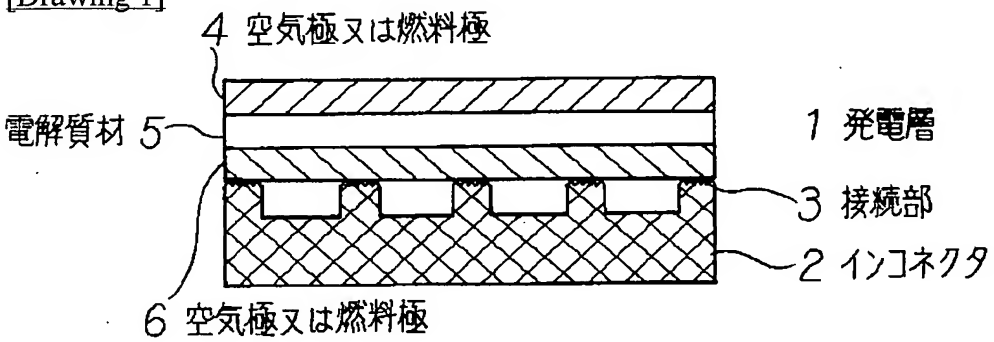
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DRAWINGS

[Drawing 1]



[Translation done.]